

WE START WITH YES.



# Fluorinated Solvent-Based Electrolytes for Low Temperature Li-ion Battery

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**Project ID: BAT525**

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# OVERVIEW

## Timeline

- Start: October 1, 2019
- End: September 30, 2022
- Percent Complete: 80%

## Budget

- Total project funding for FY22:
- DOE: \$600,000

## Barriers

- Electrolyte with improved low temperature performance for PHEV and EV battery that meets or exceeds the goal of DOE and US DRIVE
- Improve abuse tolerance of EV battery

## Partners

- Lawrence Berkeley National Laboratory (LBL)
- Pacific Northwest National Laboratory (PNNL)
- Leading Organization:  
Argonne National Laboratory (ANL)

# RELEVANCE AND PROJECT OBJECTIVES

- The next-generation EV battery requires not only high-energy density, high-power density, long cycle and calendar life, low cost with enhanced safety, but also superior low temperature (LT) performance, especially in the cryogenic range from -20°C to -40°C, and fast charging capability.
- New electrolytes with significantly improved low temperature performance is critically needed to solve the performance degradation problem of lithium-ion battery (LIB) at cryogenic temperature.
- Current LIB using traditional EC-based electrolyte experiences significant capacity (60% loss at -40°C) and energy loss when operated at low temperatures.
- Non-traditional electrolytes with extremely low melting point (m.p.), high Li<sup>+</sup> diffusivity, less resistant solid-electrolyte-interface (SEI) and low charge transfer impedance are urgently needed.
- DOE objectives for advancing the EV battery with improved LT performance, which if successful will help expand proliferation of LIB systems to greater geographical areas.
- Improved LT performance is highly relevant especially as EVs become closer to large-scale market adoption.

## Project Objectives

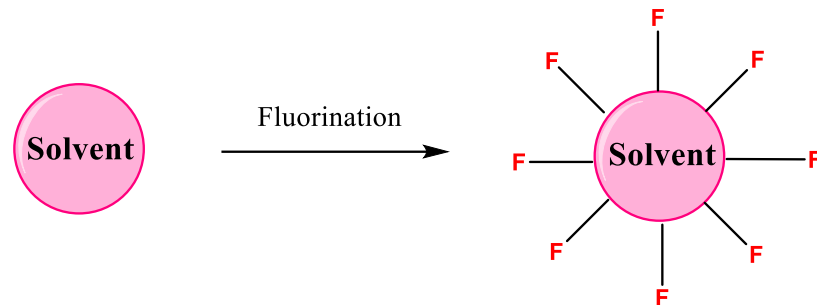
- ✓ The objective of this project is to develop next-generation electrolyte materials and formulations that could significantly improve the low temperature performance without compromising other properties such as high-temperature performance (>50°C) and fast charge capability (>6 C).

# TECHNICAL APPROACH

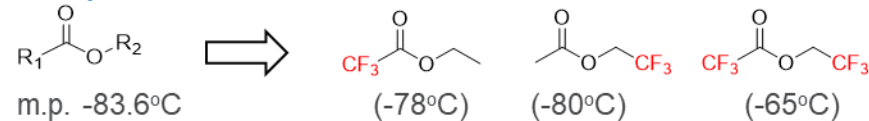
Integrated approach for new electrolyte development with theoretical modeling (DFT and MD), solvent molecular design, organic synthesis, electrolyte formulation and screening, electrochemical performance evaluation, and post-test diagnosis

Rational design of fluorinated electrolytes for low temperature lithium-ion battery:

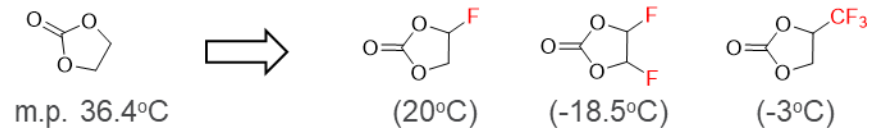
- ✓ Low m.p. solvents – extended liquid range of the electrolyte at LT
- ✓ Low Li<sup>+</sup>- binding energy – high Li<sup>+</sup> diffusivity
- ✓ Resilient SEI formation with low resistance
- ✓ Low Li<sup>+</sup>-desolvation energy – facilitated charge transfer at electrode interface at LT
- ✓ Low Li<sup>+</sup>-desolvation energy – facilitated charge transfer during charging – fast charging process
- Low HOMO energy – high oxidation stability
- Compatibility with graphite – surface passivation
- High compatibility with Li – Li metal battery



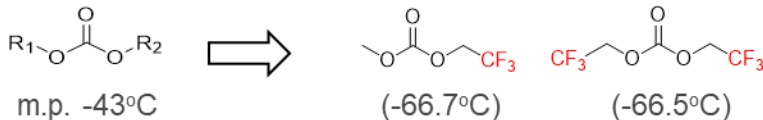
## Carboxylate Ester



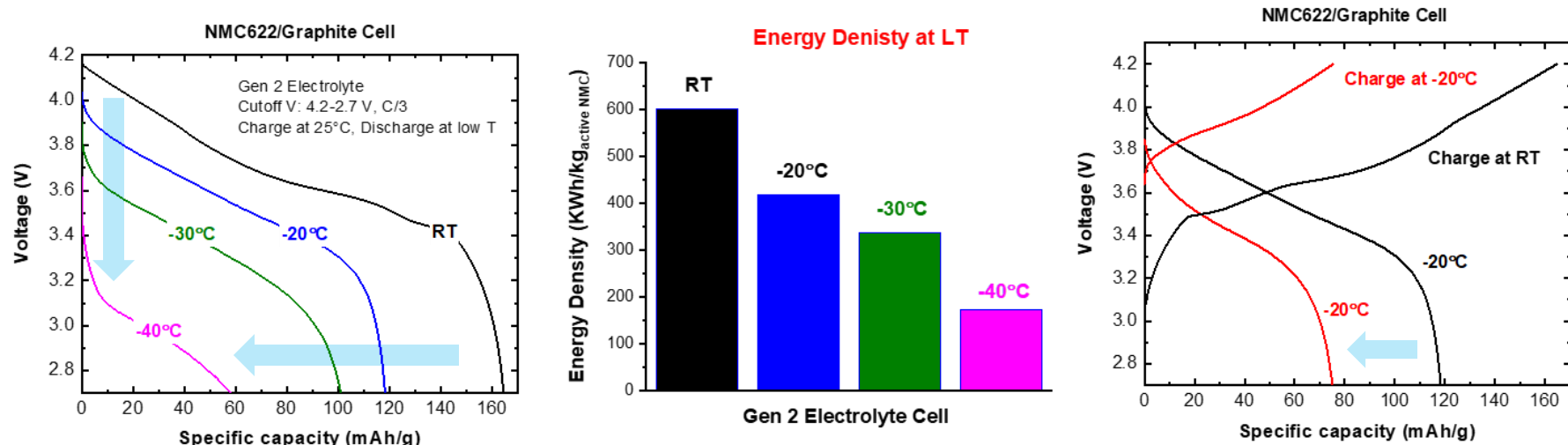
## Cyclic Carbonate



## Linear Carbonate



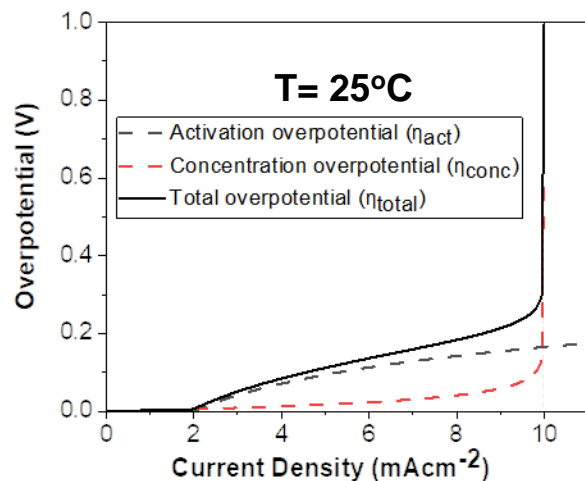
## Lithium-ion Battery Performance at Low Temperatures (<-20°C)



- ✓ Li-ion battery suffers from inferior LT performance caused mainly from the graphite negative electrode.
- ✓ Fully charged at 25°C and discharged at low temperatures (LT), NMC622/Graphite cell delivers much less discharge capacity with decreasing T. At -20°C, the discharge capacity is 70% of that at RT (= 25°C), and this value further drops to 40% when T further decreases to -40°C.
- ✓ Additionally, accounted for cell overpotential, overall cell energy decreases more dramatically compared with the discharge capacity. For example, at -40°C, cell energy is only 24% of energy achieved at RT.

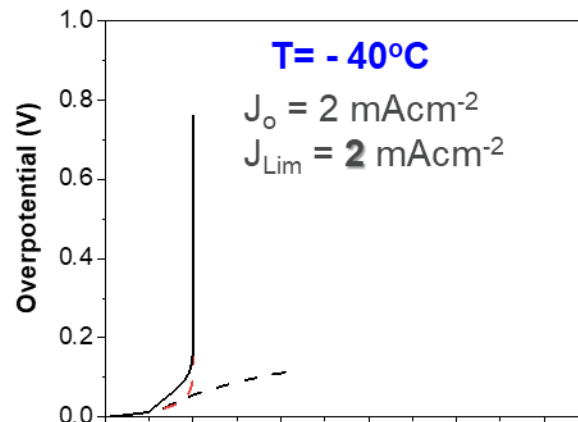
## Limiting Factors for Performance Degradation at Low Temperatures (<-20°C)

Exchange current ( $J_o$ ) = 2 mAcm<sup>-2</sup>  
Limiting current ( $J_{Lim}$ ) = 10 mAcm<sup>-2</sup>

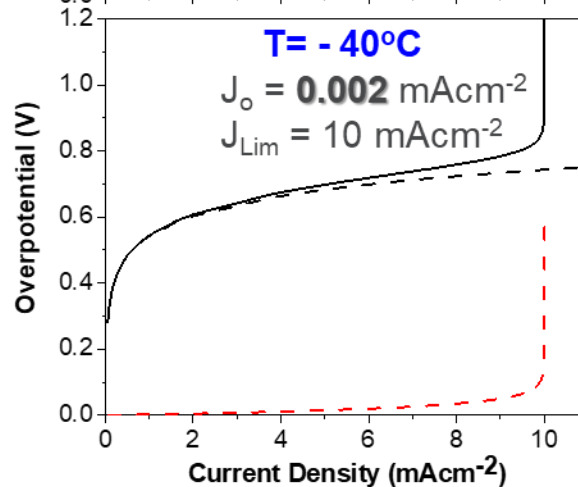


Low  $J_{Lim}$   
(Ionic conductivity)

Low  $J_o$   
(Interfacial resistance)

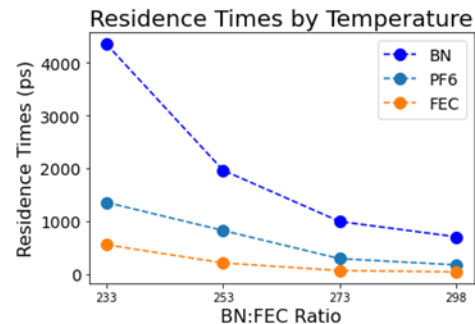
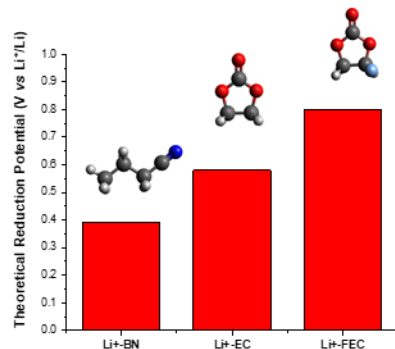
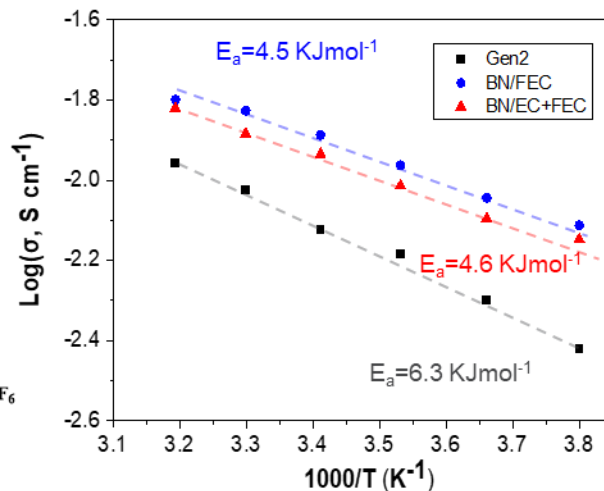
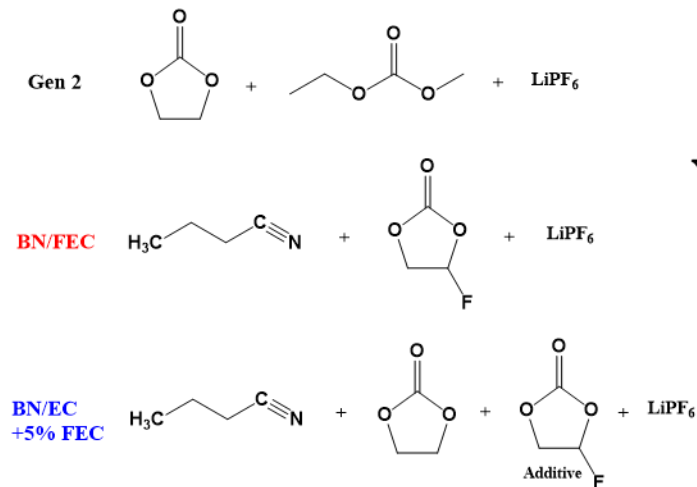


**High ionic conductivity required**



**Low interfacial resistance required**

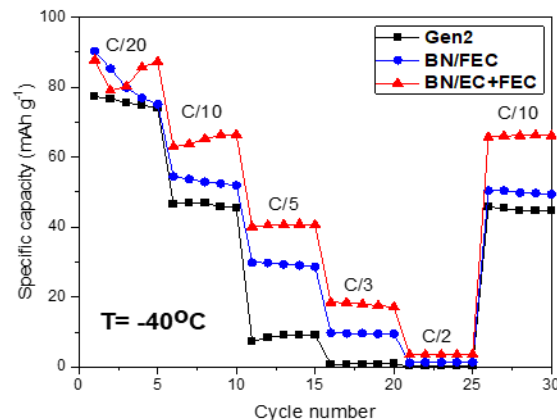
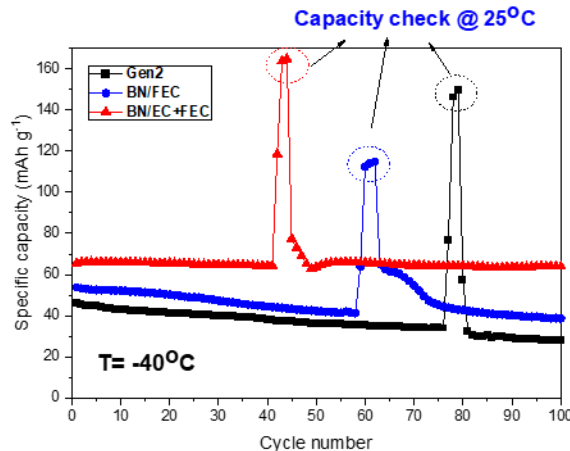
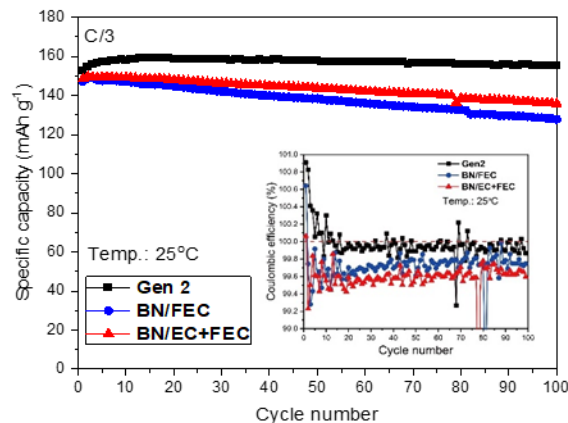
## Butyronitrile (BN)-Based Electrolytes for LT: Role of Conductivity



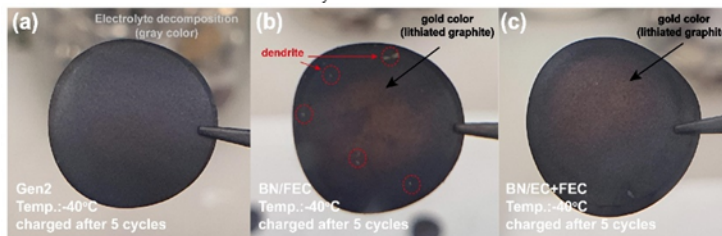
- ✓ BN has a low m.p. ( $-112^\circ\text{C}$ ) and high dielectric constant ( $\epsilon=24.8$ ). Its conductivity ( $\sigma$ ) is 10 times higher than that of Gen 2.
- ✓ BN coordinates with  $\text{Li}^+$  strongly via N ( $-\text{CN}$ ) and dominates the solvation shell, excluding other solvents and the anion.
- ✓ EC and FEC are coordinated via O ( $-\text{C}=\text{O}$ ), but much weaker than the N ( $-\text{CN}$ ) in BN.
- ✓ Residence time dramatically increases as T drops, allowing FEC and  $\text{PF}_6^-$  to participate in the solvation shell more frequently.

## Highly Conductive BN-Based Electrolytes: Low Temperature Performance

NMC622/graphite cell performance at (a) 25°C and (b) -40°C with different electrolytes; (c) C-rate capability at -40°C



Graphite anode  
(fully charged)

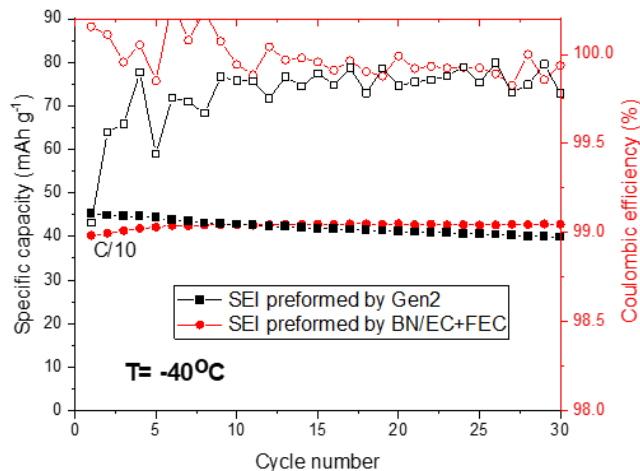


- ✓ At room temperature, BN/FEC and BN/EC+FEC electrolyte cells suffer from a slight capacity fade (86% and 91% in 100 cycles) compared with Gen 2 of 98%, indicating continuous BN solvent reduction occur during cycling.
- ✓ However, at low temperature -40°C, BN/EC+FEC electrolyte showed remarkable capacity retention compared with Gen 2 (98% vs 61%) due to its low overpotential at the anode resulting in less lithium plating.

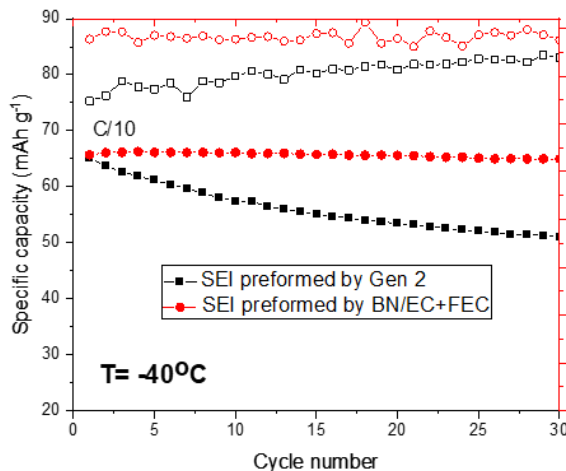


# Highly Conductive BN-Based Electrolytes: Role of SEI for LT Performance

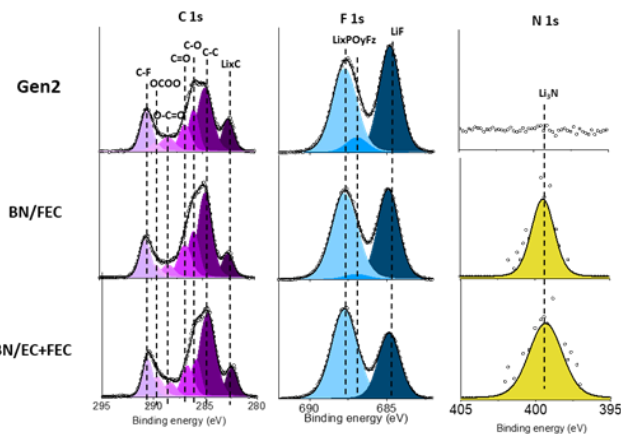
SEI Preformed  
Cycled with **Gen 2** electrolyte



SEI Preformed  
Cycled with **BN/EC+FEC** electrolyte

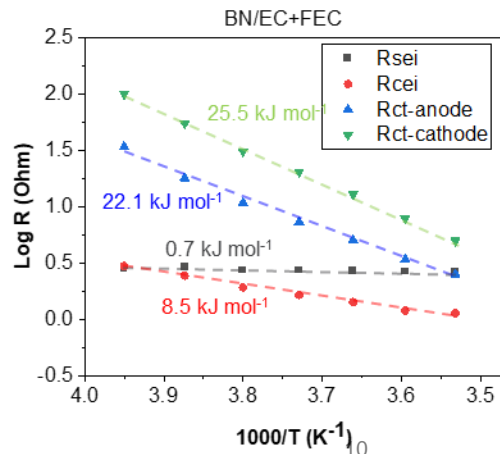
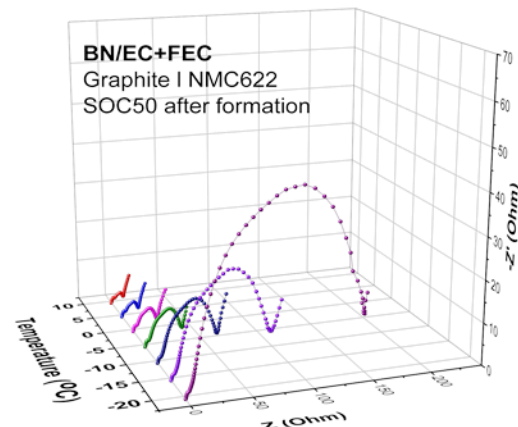
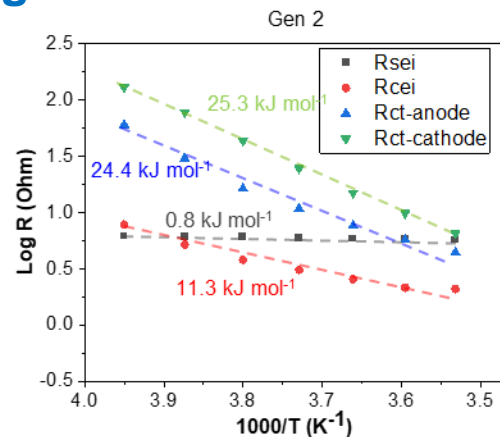
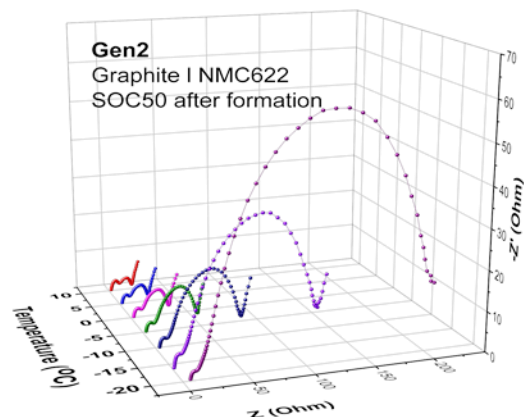


C<sub>1s</sub>, F<sub>1s</sub> and N<sub>1s</sub>  
XPS spectra of graphite anode



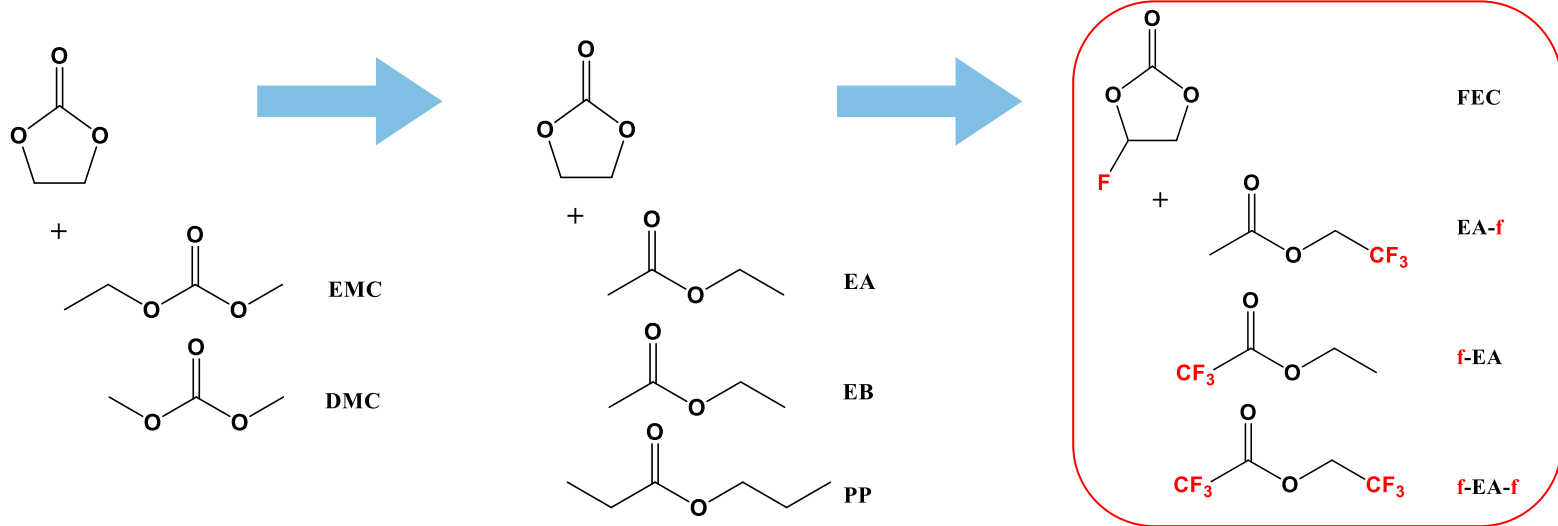
- ✓ SEI preformed by BN/EC+FEC improves the low temperature performance.
- ✓ The impact of BN/EC+FEC preformed SEI on LT performance is more significant when coupled with the highly conductive BN/EC+FEC electrolyte.
- ✓ XPS spectra showed the presence of Li<sub>3</sub>N in the SEI layer for both BN/FEC and BN/EC+FEC cells, indicating not only highly conductive electrolyte, but a more conductive SEI is also critical for low temperature performance.

## SEI and Interfacial Charge Transfer Resistance by Impedance Spectroscopy



- Nyquist plots of NMC622/graphite cells with
- Gen 2, and BN/EC + FEC electrolytes at various low temperatures (*right*)
- Arrhenius plots of  $R_{SEI}$ ,  $R_{CEI}$ ,  $R_{ct-anode}$  and  $R_{ct-cathode}$  for cells with Gen 2, and BN/EC + FEC electrolytes (*left*)
- At each low temperature, BN/EC + FEC electrolyte cells showed smaller  $R_{SEI}$ ,  $R_{CEI}$ ,  $R_{ct-anode}$  and  $R_{ct-cathode}$  compared to Gen 2 cell.
- Considering the overpotential on graphite anode is a limiting factor at low temperature, the significantly lower  $R_{ct-anode}$  activation energy of BN/EC + FEC enables cycling performance and C-rate capability at low temperature.

## Fluorinated Ester-Based Electrolytes: Role of $\text{Li}^+$ - Desolvation Energy



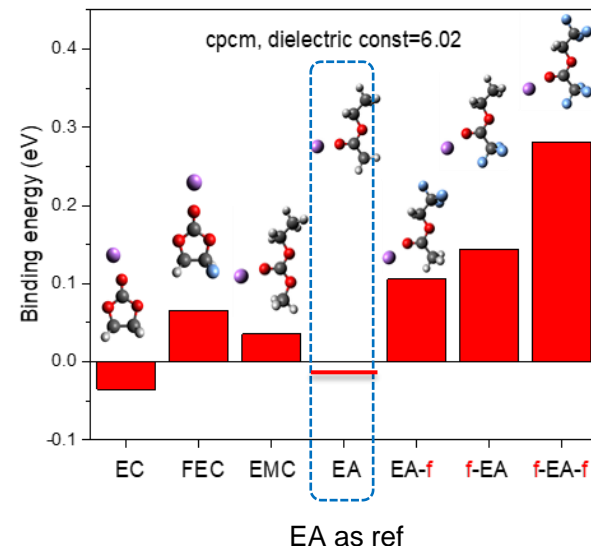
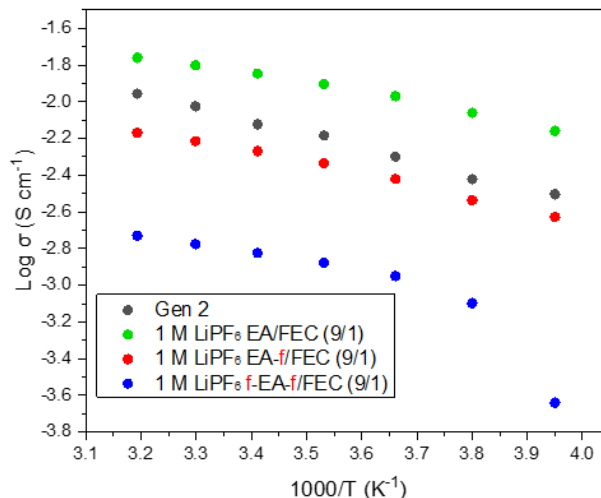
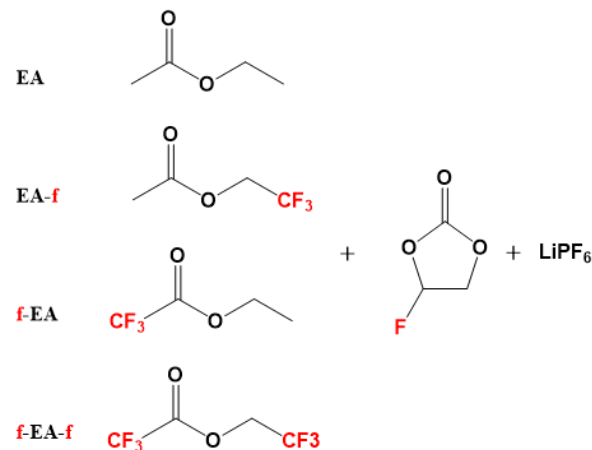
- High melting point
- Low conductivity at low  $T$
- Poor LT performance
- Poor HT performance

- Low melting point
- High conductivity at low  $T$
- Good LT performance
- Poor HT performance

- Low melting point
- Conductivity equivalent to Gen2 at low  $T$
- Low  $\text{Li}^+$  - desolvation energy
- High oxidation stability
- Non-flammability

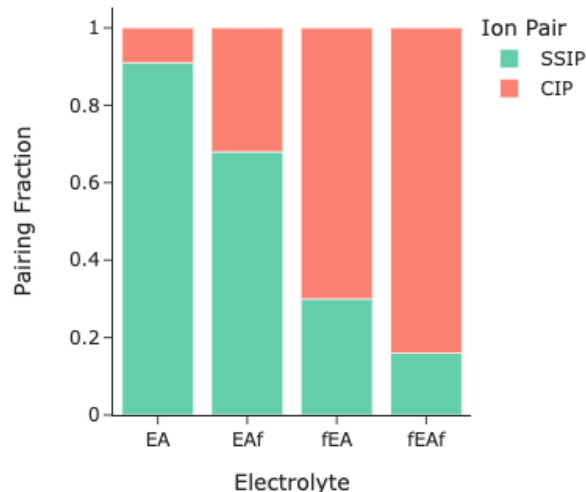
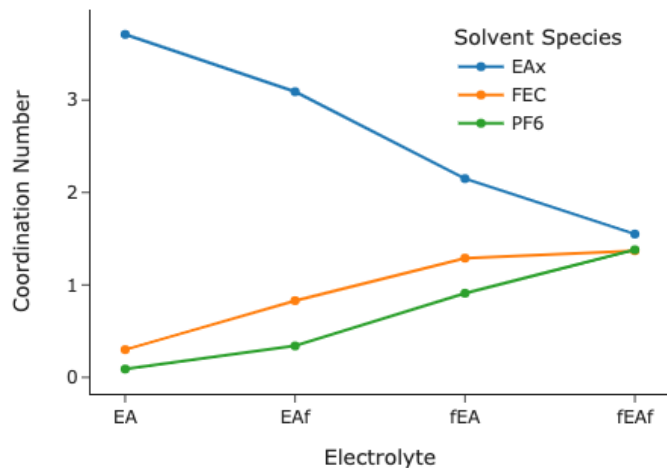
- ✓ Transition from traditional carbonate-based electrolytes to fluorinated ester-based electrolytes.
- ✓ The role of  $\text{Li}^+$ - desolvation energy in low temperature performance.
- ✓ Effect of position and degree of fluorination on low temperature, high temperature performance and fast charge.

## Fluorinated Ester-Based Electrolytes: Formulation, Conductivity & Li<sup>+</sup> Binding E

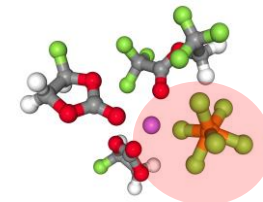


- ✓ Fluorinated ester-based electrolytes were formulated with 10% FEC as an additive and 1 M LiPF<sub>6</sub> as salt.
- ✓ High fluorination degree decreases the ionic conductivity due to the formation of high concentration of contact ion pairs (CIP).
- ✓ EA-f electrolyte is the most conductive among all fluorinated ester electrolytes.
- ✓ Li<sup>+</sup> binding energy decreases with increasing fluorination – EC > EA > EA-f > f-EA > f-EA-f.

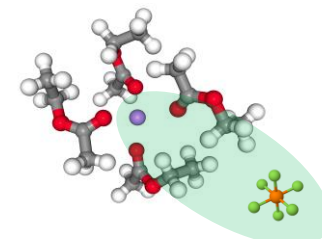
## Fluorination of Esters Reduces Li<sup>+</sup>- Solvating Power



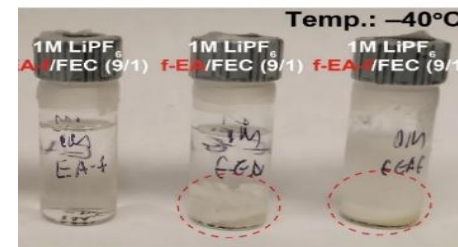
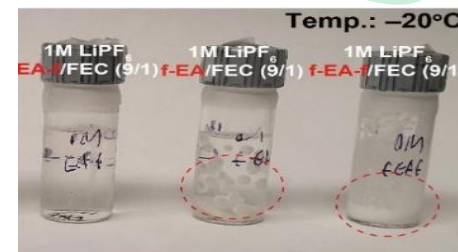
Contact Ion Pair (CIP)



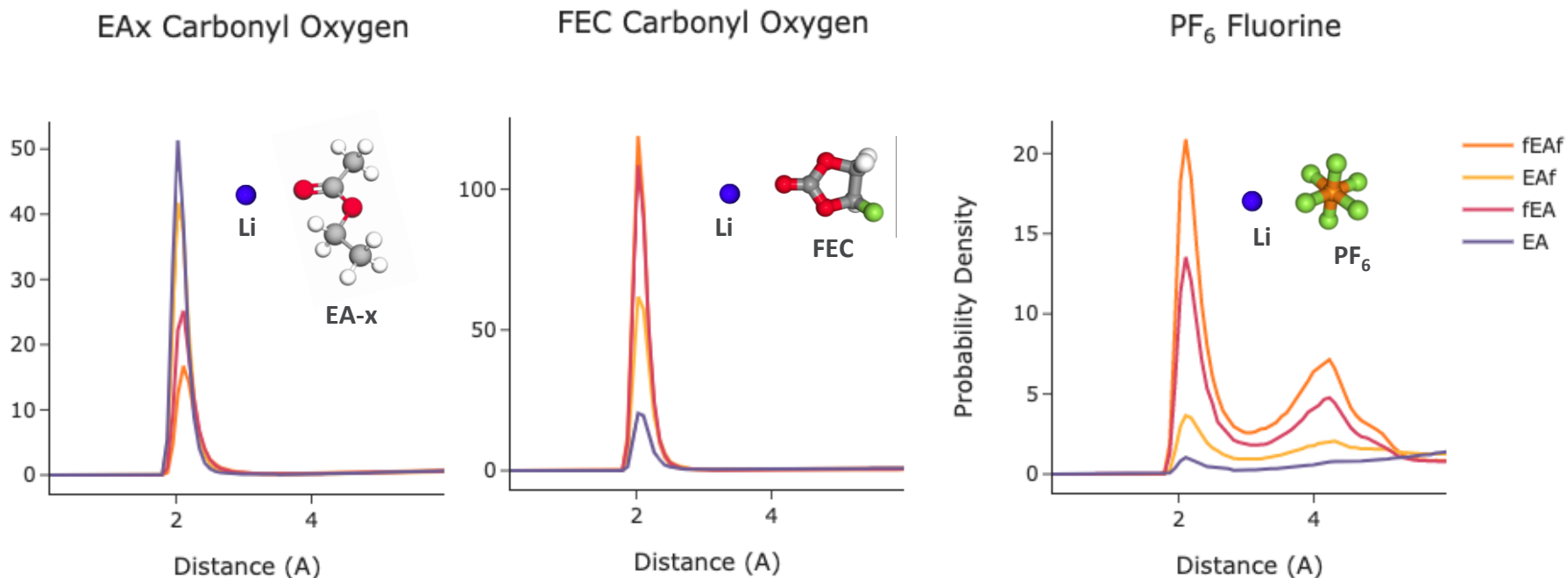
Solvent Separated Ion Pair (SSIP)



- ✓ Increasing fluorination of EA-x decreases solvating strength with Li<sup>+</sup>  
- EA < EA-f < f-EA < f-EA-f
- ✓ With increasing fluorination, Li<sup>+</sup>-EA-x solvation shell becomes more balanced.
- ✓ Weaker binding of f-EA and f-EA-f created more space for FEC and PF<sub>6</sub><sup>-1</sup> solvation, leading to the formation of more contact ion pairs (CIP).
- ✓ At RT, fluorinated esters can dissolve 1 M LiPF<sub>6</sub> salt; however, at -20°C and -40°C, LiPF<sub>6</sub> salt precipitates out from the f-EA and f-EA-f solution.
- ✓ EA-f exhibits the optimal low temperature property for LT cell<sub>3</sub> performance testing.



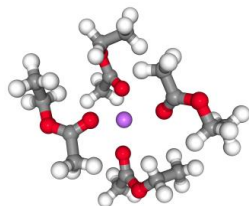
## Li RDF Calculation Demonstrates Altered Li<sup>+</sup> Solvation Structure for F-Esters



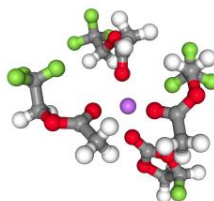
- ✓ With increasing fluorination, PF<sub>6</sub> and FEC spend more time near lithium, EA-x spends less.
- ✓ Li<sup>+</sup>-desolvation energy for the fluorinated EA-f, f-EA and f-EA-f electrolytes is anticipated to be lower than that of the non-fluorinated EA.

## Fluorination of Esters Makes Solvation Structure More Diverse

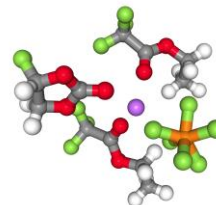
Most Common  
Solvation Shell  
in each EL



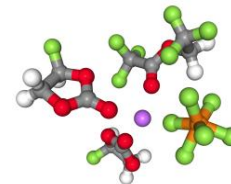
EA<sub>4</sub> : 55%



EA-f<sub>3</sub> FEC<sub>1</sub> : 25%

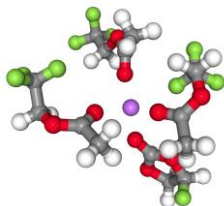


f-EA<sub>2</sub> FEC<sub>1</sub> PF6<sub>1</sub> : 17%

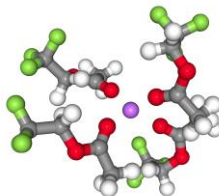


f-EA-f<sub>1</sub> FEC<sub>2</sub> PF6<sub>1</sub> : 12%

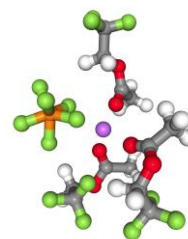
EA-f Solvation Speciation



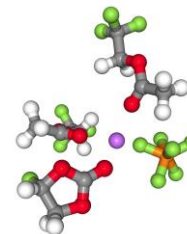
EA-f<sub>3</sub> FEC<sub>1</sub> : 25%



EA-f<sub>4</sub> : 18%



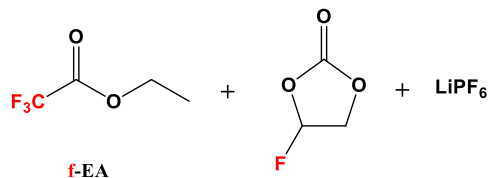
EA-f<sub>3</sub> PF6<sub>1</sub> : 12%



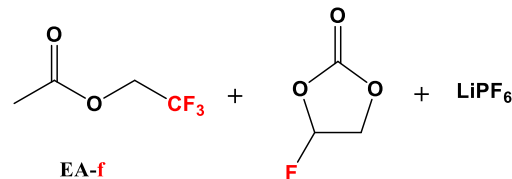
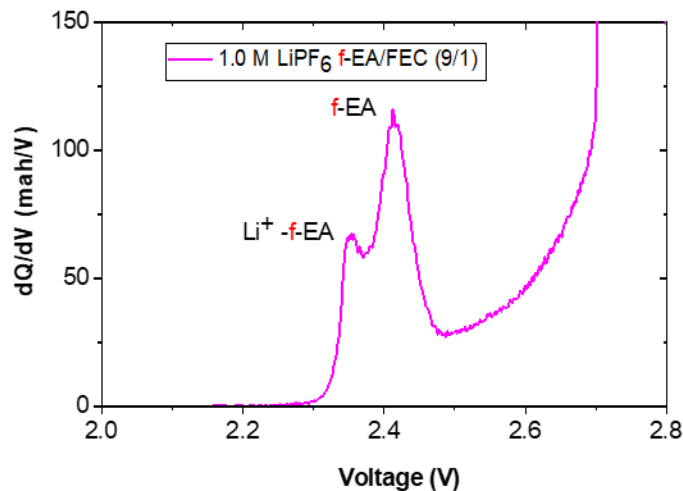
EA-f<sub>2</sub> FEC<sub>1</sub> PF6<sub>1</sub> : 7%

- ✓ Without fluorine, EA dominates in the solvation sheath, requiring high energy for Li<sup>+</sup> to desolvate and intercalate into graphite.
- ✓ As the fluorination degree increases, the diversity of Li<sup>+</sup> solvation shells increases due to the weak solvating power.
- ✓ FEC and PF<sub>6</sub> anion become nearly equal shell participants for f-EA and high fluorinated f-EA-f electrolyte.

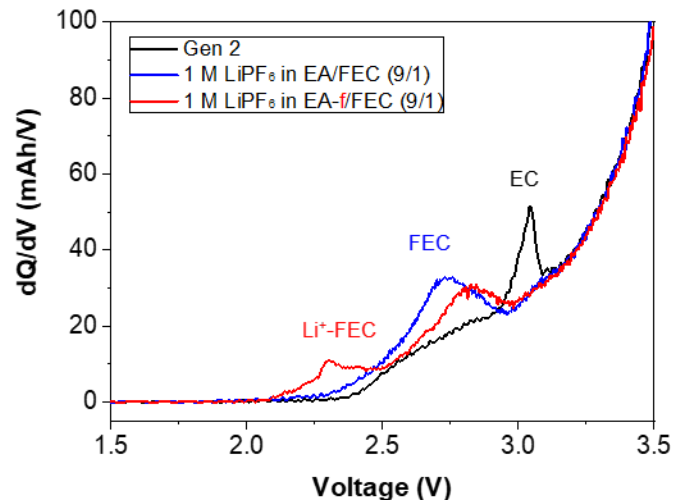
## SEI Formation On Graphite Anode Surface: F-Ester Reduction Instability



1<sup>st</sup> formation cycle, NMC622/graphite



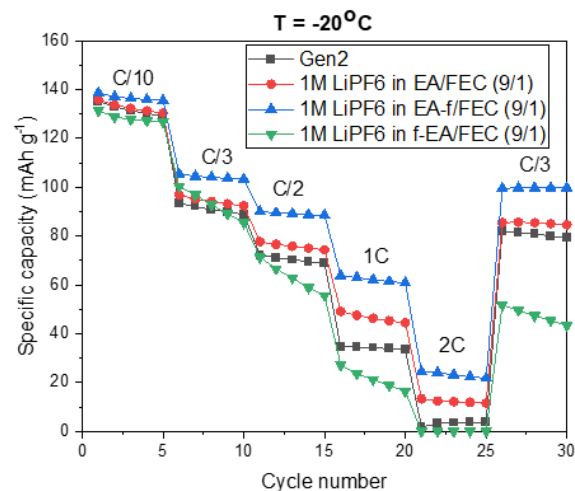
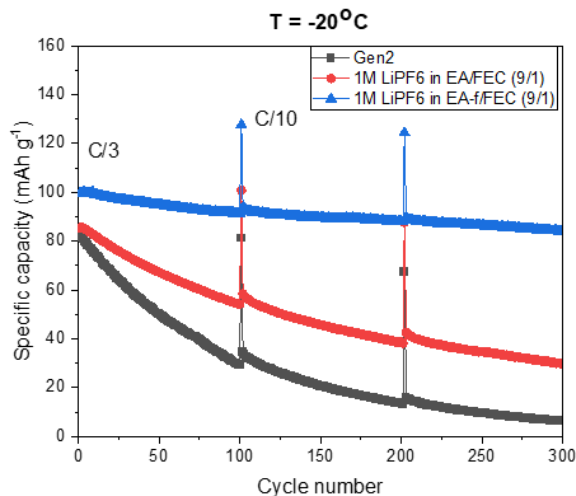
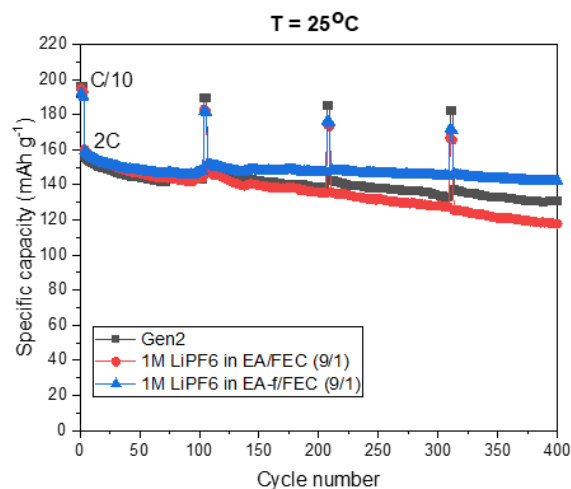
1<sup>st</sup> formation cycle, NMC622/graphite



- ✓ f-EA and f-EA-f free solvent molecules and their Li<sup>+</sup> solvated species reductively decompose without passivation, indicating lack of formation of SEI on the surface of graphite anode.
- ✓ Only EA-f/FEC electrolyte could form a good SEI *via* reduction reaction of FEC and Li<sup>+</sup> solvated FEC.
- ✓ Further optimization of SEI formation additives is ongoing.<sup>16</sup>

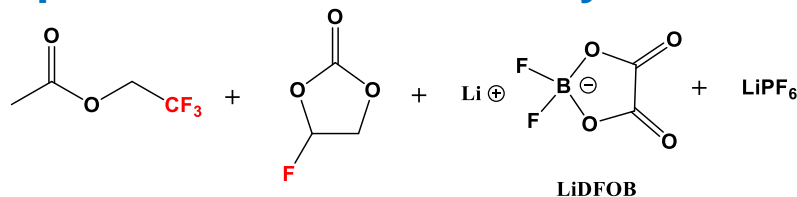


## Lithium-ion Cell Performance at Low Temperatures (<-20°C)

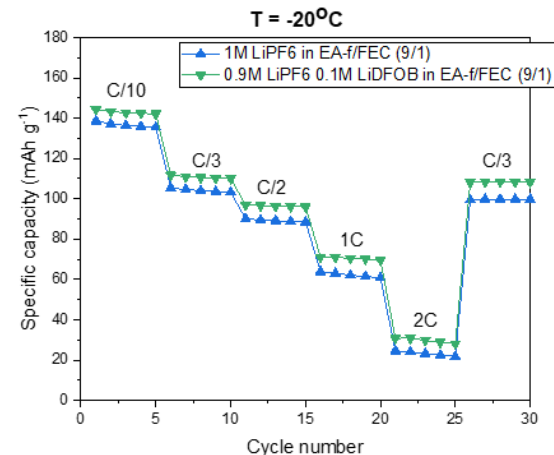
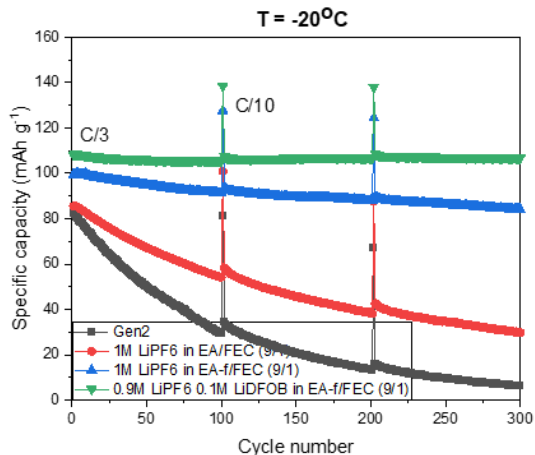
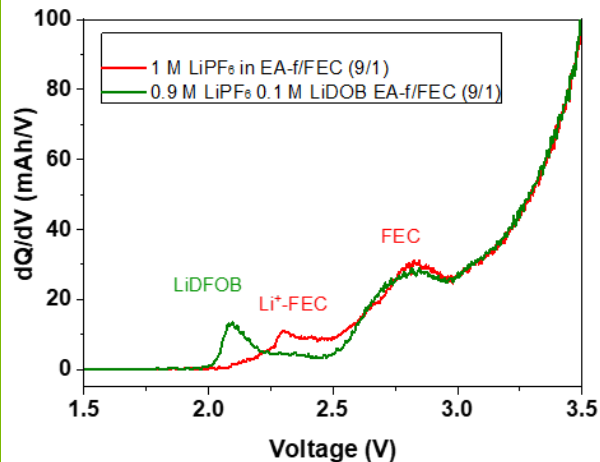


- ✓ Cycling performance and C-rate capability was tested at room temperature and -20°C using NMC622/graphite couple. The cutoff voltage is 4.4 - 2.7 V.
- ✓ At room temperature, 1 M LiPF<sub>6</sub> EA-f/FEC showed comparable cycling performance to Gen 2.
- ✓ However, when tested at -20°C, EA-f/FEC electrolyte showed much improved cycling performance and power capability than the non-fluorinated EA and SOA Gen 2 electrolyte.
- ✓ Low Li<sup>+</sup>-desolvation energy contributes to the low temperature performance.

## Further Improve Low Temperature Performance by Co-Additive

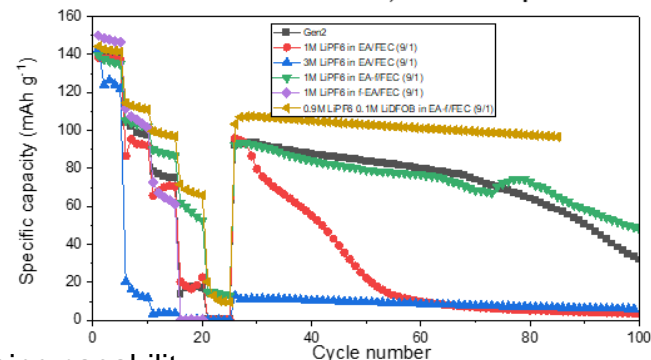
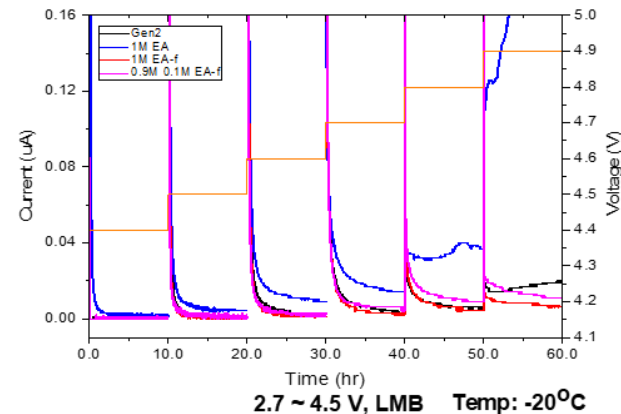
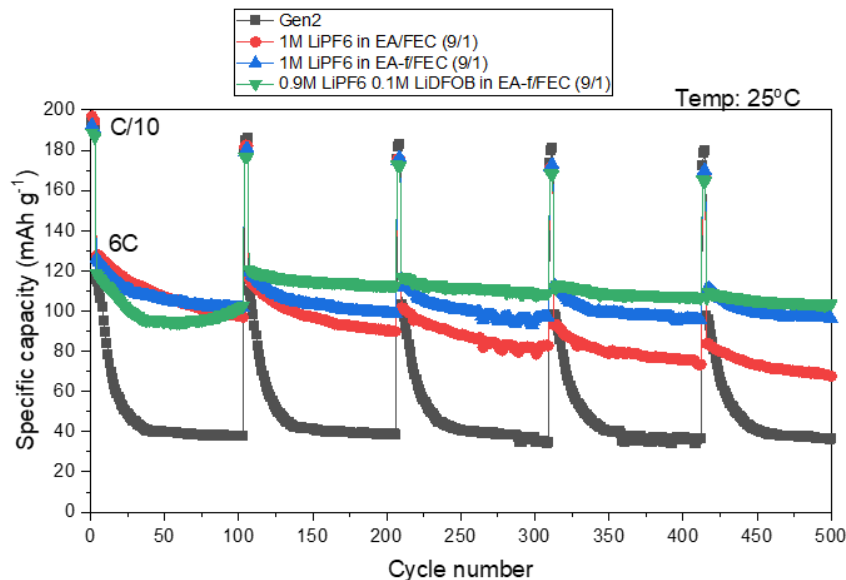


NMC622/graphite, 1<sup>st</sup> formation cycle



- ✓ Co-additive LiDFOB participates in the SEI formation together with FEC during the initial formation cycle.
- ✓ Improved SEI could further improve the low temperature cycle life and C-rate capability.
- ✓ For fluorinated EA-f electrolyte, ionic conductivity of the electrolyte is not the dictating factor; instead, low Li<sup>+</sup>-desolvation energy and low impedance SEI are.

## Fluorinated Ester Electrolyte: Fast Charging & High Voltage Capability



- ✓ As expected, low Li<sup>+</sup>-desolvation energy is also beneficial to fast charging capability.
- ✓ EA-f/FEC+LiDFOB electrolyte showed excellent fast rate cycling (6 C charge and 6 C discharge).
- ✓ Due to fluorination, EA-f/FEC electrolyte is more oxidative stable than EA and Gen 2 electrolyte.
- ✓ Fluorinated ester-based electrolyte is highly compatible with high voltage lithium metal battery.

# RESPONSE TO PREVIOUS YEAR REVIEWER'S COMMENTS

*Question 1: What seems to be missing at this early stage is an emphasis on determining the origins of poor Li-ion cell performance at lower temperatures, as this is not simply a function of transport properties (diffusivity and conductivity) over the temperature regime.*

Following the reviewer's comment, we have performed the analysis of limiting factors for the low temperature performance in this year's presentation. As shown in the slide 4 and slide 7, the poor LT performance is not only determined by the transport properties of electrolyte, i.e., ion diffusion coefficient and ionic conductivity, but also is heavily dependent on the mass and charge transfer resistance at the electrode interface. This results direct us to tackle the issue of LT performance of lithium-ion battery from brand new angles.

*Question 2: The reviewer said the team should provide electrode loading to show that the good results were not due to thin light-loading electrodes.*

All electrodes were provided by CAMP facility at Argonne National Laboratory. Specifically, the cathode used is NMC622 (A-C023) with a loading of  $9.48 \text{ mgcm}^{-2}$  ( $1.69 \text{ mAhcm}^{-2}$ ); the anode is graphite (A-A005B) with a loading of  $6.38 \text{ mgcm}^{-2}$  ( $1.93 \text{ mAhcm}^{-2}$ ); N/P ratio is 1.14. Apparently, these are not the thin light-loading electrodes in order to show better performance.

*Question 3: The reviewer pointed out that 25% FEC is used here, which industry indicates is not possible in large pouch cells due to gassing. Industry limits FEC content to 2%–4% due to gassing.*

We realized the issue of too much FEC used in the LT electrolyte formulation. For the new electrolyte development, we have reduced FEC content to additives level which is only 10%. Additionally, alternative additive such as LiDFOB has been employed, and the data has shown significant improvement in LT cycling performance due to the formation of more conductive SEI layer on anode. We will attempt to further reduce the FEC content to  $< 4\%$ .

*Question: The reviewer remarked per the team's stated objective to develop electrolytes that perform equally well at HT and LT, some future efforts need to be devoted to quantifying HT degradation of optimized LT electrolytes.*

In last year's presentation, we didn't cover the high temperature performance because the low temperature performance of these didn't show much improvement over the SOA electrolyte. Following the reviewer's comments, we started HT evaluation of BN/EC+FEC and EA-f/FEC + LiDFOB formulation at  $40^\circ\text{C}$  and  $55^\circ\text{C}$ , the best-performing LT electrolytes, and the preliminary cell performance looks promising.

# COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

Kristin Persson

**Lawrence Berkeley National Laboratory**

DFT calculation and molecular dynamics simulations for electrolyte

Andrew Jansen

**CAMP facility at Argonne National Laboratory**

NMC622 and graphite electrode supply

Surya Moganty

**NOHMs Technologies**

Electrolyte commercialization partner

James Dong

**Navitas Systems**

Electrolyte commercialization partner

Sheng S. Zhang

**US Army Research Laboratory**

Technical discussions

# REMAINING CHALLENGES AND BARRIERS

- While fluorinated EA-f solvent clearly shows improved LIB performance at LT, deep understanding of the interplay between solvation structure,  $\text{Li}^+$ -desolvation energy,  $\text{Li}^+$  diffusivity, SEI resistance and charge transfer impedance and new characterization technique to decouple the role of each impact are needed.
- While fluorinated EA-f improves high temperature performance over their non-fluorinated ester counterpart EA, it still suffer from rapid capacity fade same as Gen 2 electrolyte. Improving the SEI stability by developing tailored new additives are needed for both LT and HT cell performance.
- Development of effective predictors/descriptors of electrolyte performance from first-principles calculations –  $\text{Li}^+$ -desolvation energy, SEI chemical composition and their hierarchical distribution on the electrode surface – remains a challenge.
- The underlying link between electrolyte property and its low performance needs further understood – sporadic research, lack of unanimous conclusion.

# PROPOSED FUTURE RESEARCH

**Further formulation and optimization of non-traditional electrolytes for improved low temperature (-40°C ~ -20°C) and high temperature (40°C ~ 60°C) performance**

✓ **Continue working on highly conductive electrolytes with focus on**

- Liquid-solid phase diagram of BN/EC and BN/EC/LiPF<sub>6</sub> and optimization of BN/EC/LiPF<sub>6</sub> system.
- New additives to further improve long-term LT performance of optimized BN/EC/LiPF<sub>6</sub> electrolyte.
- Three-electrode experiments for lithium plating study at low temperatures.
- Deep understanding of the impact of electrolyte bulk property on LT performance.

✓ **Continue working on low Li<sup>+</sup>-desolvation electrolytes with focus on**

- SEI additives to improve 55°C cycling performance for EA-f/FEC/LiPF<sub>6</sub> electrolyte.
- Co-solvent for EA-f/Solvent binary or ternary system and liquid-solid phase diagram.
- Impact of lithium salt and its concentration on solvation energy and LT performance.
- Post-test analysis to identify the root cause of the degraded cell performance at low temperatures.
- Precise modeling of Li<sup>+</sup>-desolvation energy and Li<sup>+</sup> intercalation kinetics at SEI.
- Streamline modeling workflow to enable high-throughput classical modeling work that spans the range of experimental studies.

Any proposed future work is subject to change based on funding levels

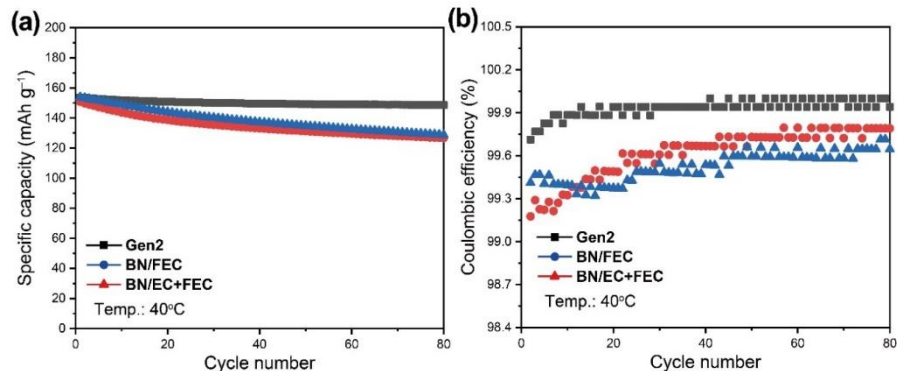
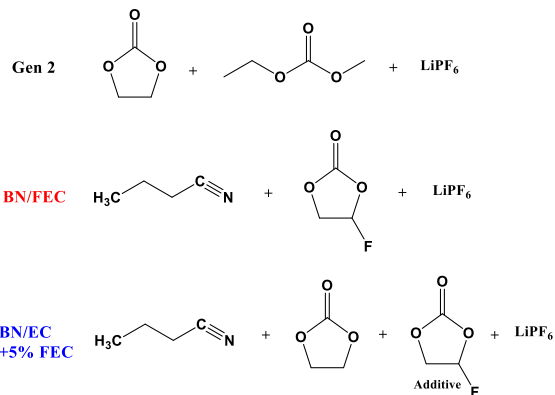
# SUMMARY

- Non-traditional fluorinated solvent-based electrolytes have been developed for low temperature lithium-ion battery demonstrated in NMC622/graphite cell.
- 2,2,2-Trifluoroethyl acetate (EA-f)/FEC with co-additive LiDFOB exhibits superior cell performance at -20°C and -40°C.
- Formulated fluorinated electrolyte 0.9 M  $\text{LiPF}_6$  EA-f/FEC + 0.1 M LiDFOB showed high voltage stability and high compatibility with Li metal anode.
- Compared with non-fluorinated counterparts (EA, EB, MP and PP), the fluorinated ester electrolyte showed much improved high temperature cycling performance at 55°C.
- With increasing fluorination degree, the  $\text{Li}^+$  binding energy and solvating power decreases ( $\text{EA} < \text{EA-f} < \text{f-EA} < \text{f-EA-f}$ ).
- With increasing fluorination,  $\text{Li}^+$ -EA-x solvation shell becomes more balanced. Weaker solvation from f-EA and f-EA-f created more space for FEC and  $\text{PF}_6^-$  solvation, leading to the formation of more contact ion pairs (CIP) and the precipitation of lithium salt at LT.
- $\text{Li}^+$  transport/ionic conductivity, SEI formation and resistance,  $\text{Li}^+$ -solvating energy and solvation structure, and charge transfer resistance all contribute to the LT performance of LIB.

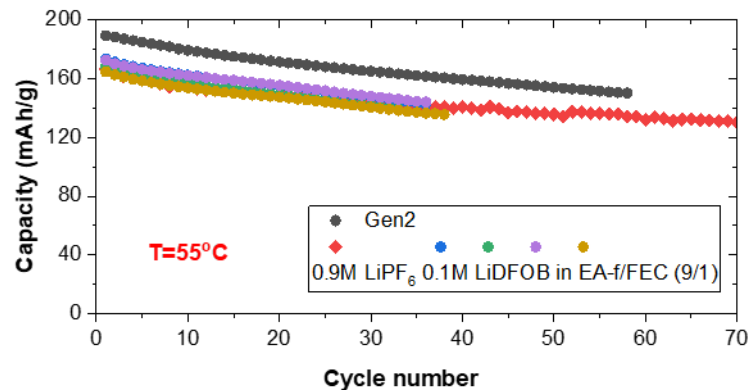
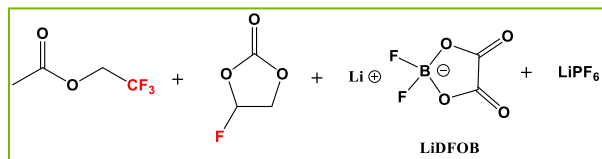


# Technical Backup Slides

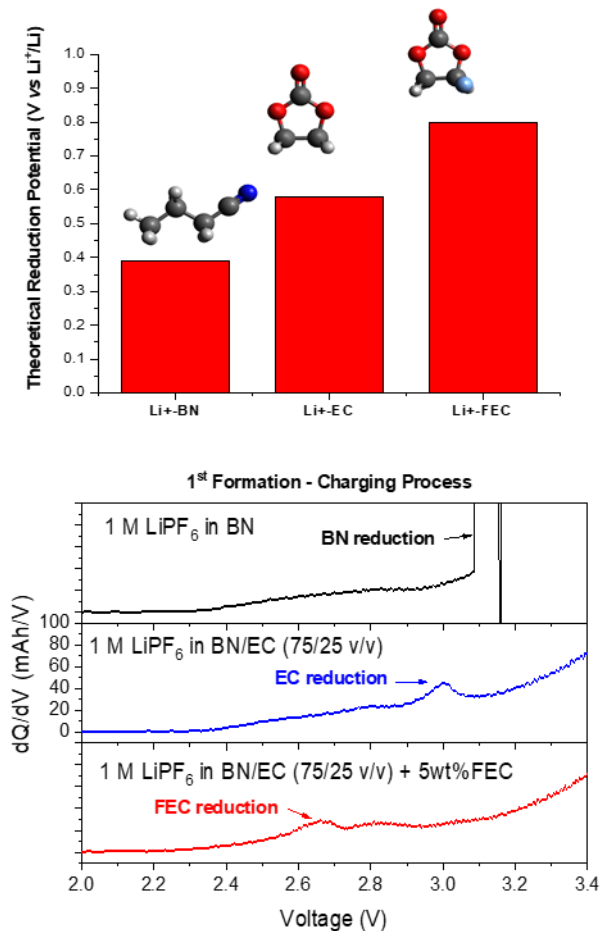
# Backup slide 1: Lithium-ion Cell Performance at High Temperatures



- NCM622, 9.48 mg cm<sup>-2</sup> (loading), 1.69 mAhcm<sup>-2</sup>
- Graphite, 6.38 mg cm<sup>-2</sup> (loading), 1.93 mAhcm<sup>-2</sup>
- N/P ratio: 1.14
- Cutoff Voltage: 4.4-2.7 V



## Backup Slide 2: BN/EC+FEC and Fluorinated Esters: f-EA, EA-f, f-EA-f

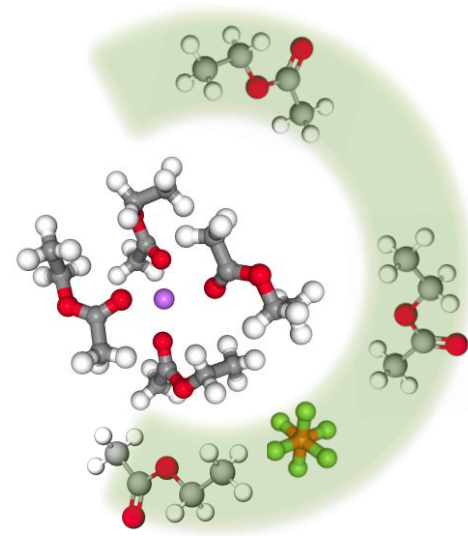
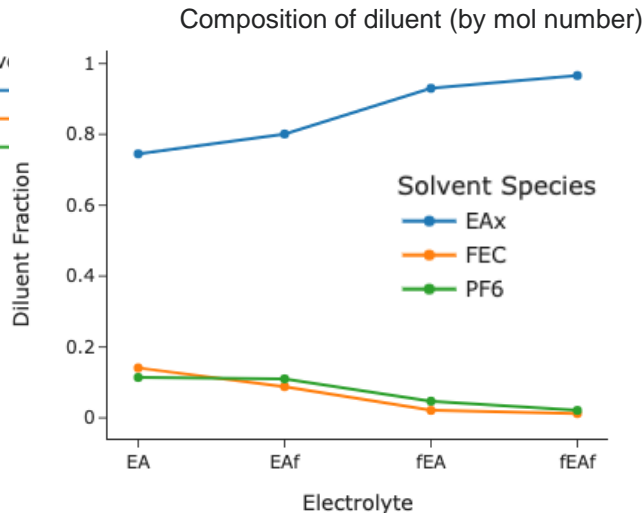
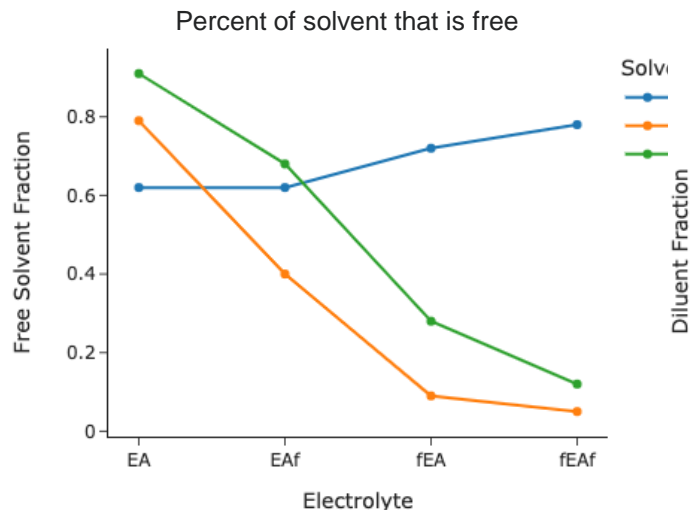


Solvent	Chemical Structure	M.P. (°C)	HOMO (eV)	LUMO (eV)	Reduction with Li <sup>+</sup> (V, Li <sup>+</sup> /Li)	Oxidation with PF <sub>6</sub> <sup>-</sup> (V, Li <sup>+</sup> /Li)
EC		36	-8.4948	-0.3135	0.86	6.39
FEC		20	-8.9754	-0.3860	1.25	7.28
EA		-83.6	-7.7004	-0.0203	0.74	6.20
f-EA		-78	-8.7868	-1.3385	1.72	7.22
EA-f		-80	-8.3862	-0.6337	1.07	6.71
f-EA-f		-65	-9.4400	-1.9447	2.09	7.42

B3LYP/6-311+g(d)  
cpcm, dielectric const.=6.02

## Backup Slide 3: Decreasing Fluorination Reshapes The Diluent

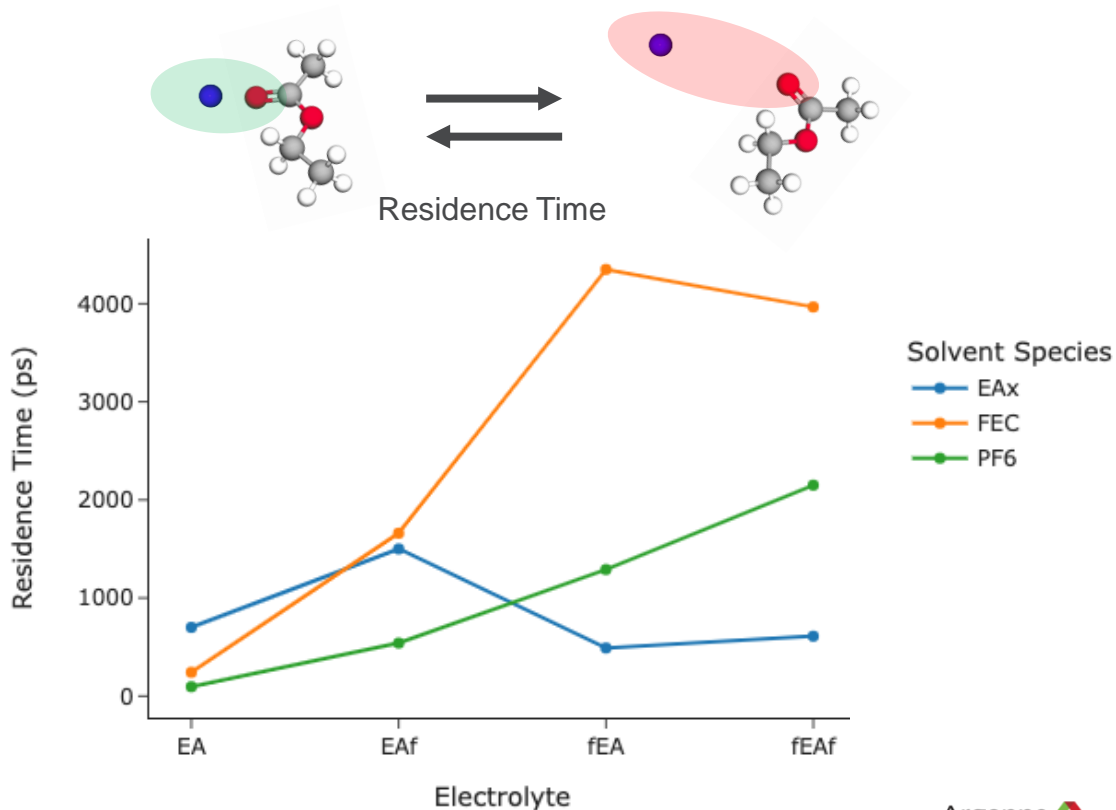
- With FEC and  $\text{PF}_6$  populating the solvation shell in f-EA and f-EA-f, very little is available in the diluent.
- Instead, the diluent becomes nearly pure fluorinated esters



the diluent is uncoordinated

## Backup Slide 4: Increasing Fluorination Alters Residence Times

- Li residence on  $\text{PF}_6^-$  anion consistently increases in the more fluorinated systems, likely due to increasing ion aggregation.
- In EA, with FEC largely excluded from the solvation shell, its residence time is very brief.
- EAF has the highest residence time of any EAx solvent. Despite weaker solvating ability, EAF is stabilizing the solvation shell.
- Residence time is calculated from the decay constant of the Li-solvent autocorrelation function



# Backup Slide 5: Charge Transfer Impedance on Both Electrodes

